

Composition-Explicit Distillation Curves of Mixtures of Diesel Fuel with Biomass-Derived Glycol Ester Oxygenates: A Fuel Design Tool for Decreased Particulate Emissions[†]

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We have recently introduced several important improvements in the measurement of distillation curves for complex fluids. The modifications provide for (1) a composition explicit data channel for each distillate fraction (for both qualitative and quantitative analysis), (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state, (3) temperature, volume, and pressure measurements of low uncertainty suitable for equation of state development, (4) consistency with a century of historical data, (5) an assessment of the energy content of each distillate fraction, (6) trace chemical analysis of each distillate fraction, and (7) a corrosivity assessment of each distillate fraction. The composition explicit channel is achieved with a new sampling approach that allows precise qualitative as well as quantitative analyses of each fraction, on the fly. We have applied the new method to the measurement of rocket propellant, gasolines, jet fuels, diesel fuels, and crude oils. In this paper, we present the application of the technique to representative batches of petroleum derived diesel fuel and mixtures of this diesel fuel with some oxygenating agents that can be derived from biomass. The distillation curve data that are presented can be used for thermodynamic modeling of these complex fluids. Moreover, we present not only the distillation curves but also a chemical characterization of each fraction and discuss the contrasts between the various mixtures.

Introduction

Diesel engine designers have increasingly come under pressure to improve environmental performance. Although very efficient, diesel engines have had difficulties achieving desirable emission targets, especially for soot and NO_x formation. Over the years, improvements have been made in the design of fuel systems, combustion chambers, and engine control. Indeed, catalytic aftertreatment of diesel exhaust has become common in large power plants. More recently, reformulation of diesel fuel has been given renewed attention.^{1–6} This has focused on two aspects of the fuel: (1) reformulation to lower the sulfur specification and (2) reformulation to incorporate oxygenates into the fuel.^{7–11}

The first aspect (lowering the sulfur specification) is more related to issues of acid precipitation rather than to soot and NO_x formation. Indeed, this goal has substantially been met as of 2007, with the introduction of ultralow sulfur diesel fuels that meet the target 15 ppm (mass/mass) specification. The second goal, on the other hand, is still the subject of research.¹²

Reformulation of diesel fuel to include oxygenates has proven to be an effective way to reduce soot and NO_x emissions, to enhance the ability to recirculate exhaust gases (EGR), to reduce in-cylinder radiative heat transfer (and thereby improve efficiency), and may enable the application of more sophisticated

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aftertreatment technologies. There are indications that it might be possible to produce completely smoke-free operation of a diesel engine by the incorporation of 38% (mass/mass) of oxygen into the fuel.¹³ Since the reformulation is usually done by mixing oxygenates directly into the diesel fuel, such reformulations are applicable to biodiesel as well. Four major classes of chemical additives have been considered for diesel oxygenates: alcohols, ethers, glycol ethers, and glycol esters.^{14–29} For a variety of reasons, the glycol ethers and glycol esters have emerged as among the most promising.^{18,30} These compounds have been extensively studied for their solvent properties, so a great deal is known about their properties and behavior.^{18,31} Moreover, there have been several studies of diesel fuel

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Table 1. Some Representative Properties of the Oxygenating Fluids Studied in This Work^{48–50}

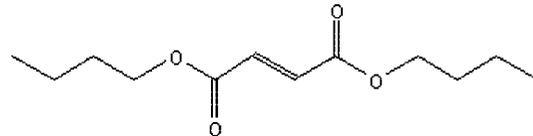
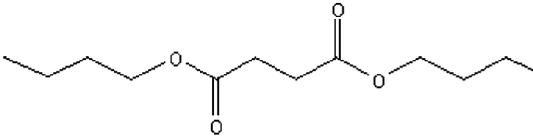
Dibutyl Fumarate	
	
CAS No. 105-75-9	
InChI = 1/C ₁₂ H ₂₀ O ₄ /c1-3-5-9-15-11(13)7-8-12(14)16-10-6-4-2/h7-8H,3-6,9-10H2,1-2H3/b8-7+	
RMM = 228.28	
<i>T</i> _{boil} = 276.9 °C (predicted with TDE)	
<i>T</i> _{fus} = −18.2 °C	
density = 0.987 g/mL (20 °C)	
refractive index, <i>n</i> _D ²⁰ = 1.4457 (25 °C)	
synonyms: 2-butenedioic acid (e), dibutyl ester, dibutyl ester fumaric acid, butyl fumarate, dibutyl fumarate, di- <i>n</i> -butyl fumarate, dibutyl (2E)-2-butenedioate, DBF	
Dibutyl Succinate	
	
CAS No. 141-03-7	
InChI = 1/C ₁₂ H ₂₂ O ₄ /c1-3-5-6-15-11(13)7-8-12(14)16-10-6-4-2/h3-10H2,1-2H3	
RMM = 230.30	
<i>T</i> _{boil} = 274.6 °C	
<i>T</i> _{fus} = −29.0 °C	
density = 0.985 g/mL (20 °C)	
refractive index, <i>n</i> _D ²⁰ = 1.4291 (25 °C)	
synonyms: butanedioic acid, dibutyl ester, succinic acid dibutyl ester, di- <i>n</i> -butyl succinate, DBS	

Table 2. Summary of the Initial Behavior of the Diesel Fuel Mixtures with the Bioderivable Glycol Ether Oxygenates (With the Pure Diesel Fuel Values Provided for Reference)^a

observed		75/25	50/50	25/75
temperature	diesel	diesel/DBF	diesel/ DBF	diesel/ DBF
(°C)	(83.51 kPa)	(83.47 kPa)	(83.72 kPa)	(83.82 kPa)
vapor rising	233.4	240.1	248.5	260.8
observed	diesel	75/25	50/50	25/75
temperature	(83.51 kPa)	diesel/DBS	diesel/DBS	diesel/DBS
(°C)		(83.12 kPa)	(83.37 kPa)	(83.42 kPa)
vapor rising	233.4	235.4	248.2	259.4

^a The vapor rise temperature is that at which vapor is observed to rise into the distillation head, considered to be the initial boiling temperature of the mixture. These temperatures have been corrected to 1 atm with the Sydney Young equation; the experimental atmospheric pressures are provided to allow recovery of the actual measured temperatures. The uncertainties are discussed in the text.

oxygenated with glycol ethers and glycol esters in research engines, described in many of the studies cited above.

In a previous paper, we presented the results from the advanced distillation curve measurement metrology for diesel fuel and mixtures of diesel fuel with several glycol ether and glycol ester oxygenates.¹⁴ These compounds are of interest because they have been proven to decrease particulate production when used as diesel fuel additives. Specifically, the oxygenates studied in that work were: tri(propylene glycol) methyl ether (TPM, CAS No. 20324-33-8), dibutyl maleate (DBM, CAS No. 105-76-0), and a mixture of diethylene glycol methyl ether (DGME, diglyme, 2-methoxyethyl ether, CAS No. 111-96-6) + 1,2-dimethoxyethane (DME, monoglyme, dimethyl glycol, ethylene glycol dimethyl ether, dimethyl cellosolve, CAS

Table 3. Representative Distillation Curve Data for the Samples of Diesel Fuel and Mixtures of Diesel Fuel with Dibutyl Succinate^a

distillate volume fraction, %	diesel (83.27 kPa)		75–25 diesel–dibutyl succinate (82.50 kPa)		50–50 diesel–dibutyl succinate (82.03 kPa)		25–75 diesel–dibutyl succinate (83.50 kPa)	
	T_k , °C	T_h , °C	T_k , °C	T_h , °C	T_k , °C	T_h , °C	T_k , °C	T_h , °C
5	242.9	238.2	250.8	227.3	260.2	237.4	269.3	254.5
10	248.6	241.8	256.0	238.4	264.1	250.3	271.7	265.3
15	254.3	245.1	260.9	247.4	267.5	257.5	273.5	269.4
20	259.9	248.4	265.0	253.4	270.3	261.9	274.9	271.7
25	264.9	251.3	268.4	258.3	272.5	265.5	275.9	272.8
30	269.7	254.3	271.9	263.0	274.5	269.0	276.7	274.3
35	275.0	257.3	274.9	267.3	276.1	271.3	277.5	275.3
40	279.6	260.5	277.5	270.6	277.8	273.5	278.1	276.2
45	284.4	263.8	280.0	273.4	279.0	274.8	278.8	277.0
50	289.2	268.9	282.7	276.3	280.2	276.3	279.3	277.6
55	293.7	272.3	285.4	278.9	281.2	277.9	280.0	278.6
60	297.9	277.8	288.2	281.0	282.4	279.0	280.8	279.3
65	303.0	285.5	291.1	284.8	283.8	280.1	281.4	280.5
70	308.3	294.2	294.3	283.3	285.4	281.4	282.0	281.7
75	313.5	303.6	298.4	290.4	287.0	282.6	282.7	283.3
80	319.8	313.8	304.6	294.8	289.2	284.1	283.6	277.6
85	327.5	322.9	311.3	300.5	292.1	286.3	284.6	280.0

^a These data are plotted in Figure 2. The uncertainties are discussed in the text. These temperatures have been corrected to 1 atm with the Sydney Young equation; the experimental atmospheric pressures are provided in parentheses to allow recovery of the actual measured temperatures.

Table 4. Representative Distillation Curve Data for the Samples of Diesel Fuel and Mixtures of Diesel Fuel with Dibutyl Fumarate^a

distillate volume fraction, %	diesel (83.27 kPa)		75–25 diesel–dibutyl fumarate (82.38 kPa)		50–50 diesel–dibutyl fumarate (83.05 kPa)		25–75 diesel–dibutyl fumarate (83.75 kPa)	
	T_k , °C	T_h , °C	T_k , °C	T_h , °C	T_k , °C	T_h , °C	T_k , °C	T_h , °C
5	242.9	197.8	252.7	208.3	263.1	231.5	275.3	248.6
10	248.6	212.4	258.0	225.4	267.2	249.3	277.6	265.4
15	254.3	223.4	263.0	242.3	270.8	259.2	279.3	272.6
20	259.9	231.2	267.3	250.7	273.9	265.4	280.9	276.7
25	264.9	234.8	270.8	257.4	276.4	269.8	282.1	278.3
30	269.7	242.6	274.6	263.7	278.9	273.0	283.2	279.9
35	275.0	249.9	277.4	268.6	280.8	275.6	284.1	280.8
40	279.6	254.9	280.3	272.2	282.6	277.6	284.6	281.9
45	284.4	263.1	283.3	275.8	284.2	279.7	285.3	282.4
50	289.2	268.2	286.0	278.6	285.8	281.7	286.0	283.1
55	293.7	274.3	288.5	281.2	287.4	283.3	286.6	283.6
60	297.9	275.0	291.3	279.0	288.8	284.8	287.4	284.0
65	303.0	282.7	294.7	280.5	290.4	286.4	288.3	284.7
70	308.3	286.5	298.1	283.1	292.1	285.4	289.0	285.5
75	313.5	292.4	302.2	290.3	294.1	287.9	289.9	286.2
80	319.8	295.4	307.3	286.7	296.8	286.8	291.2	286.9
85	327.5	299.6	314.6	300.5	300.3	289.9	293.2	287.5

^a These data are plotted in Figure 1. The uncertainties are discussed in the text. These temperatures have been corrected to 1 atm with the Sydney Young equation; the experimental atmospheric pressures are provided in parentheses to allow recovery of the actual measured temperatures.

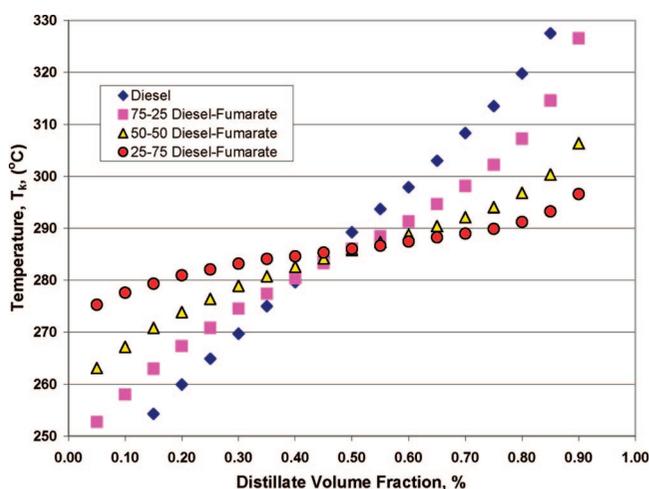


Figure 1. Distillation curves, presented in T_k , for diesel fuel and three mixtures of diesel fuel with dibutyl fumarate (DBF). The uncertainties of the measurements are discussed in the text.

is often referred to as Cetaner. While these fluids have proven to be valuable as oxygenates, they are all derived from catalytic synthesis reactions involving carbon monoxide, alcohols, and aldehydes and are therefore dependent on the availability of other commodity chemicals. Two compounds that are closely related to DBM above can be derived from biomass fermentation, however, and they might be substituted if the physical, chemical, and engineering properties are available for evaluation.³² These compounds are dibutyl fumarate (DBF, CAS No. 105-75-9) and dibutyl succinate (DBS, CAS No. 141-03-7). In this paper, we describe the application of the advanced distillation curve approach to diesel fuel mixtures with these two renewable oxygenating fluids.

The motivation for the study of the biomass derived oxygenates with conventional diesel fuel with the advanced distillation curve stems from the overarching desire to model these complex fluids with reliable equations of state. If an equation of state

No. 110-71-4). When the mixture of DGME + DME is prepared in a ratio of 80/20 (vol/vol) DGME/DME, the resulting mixture

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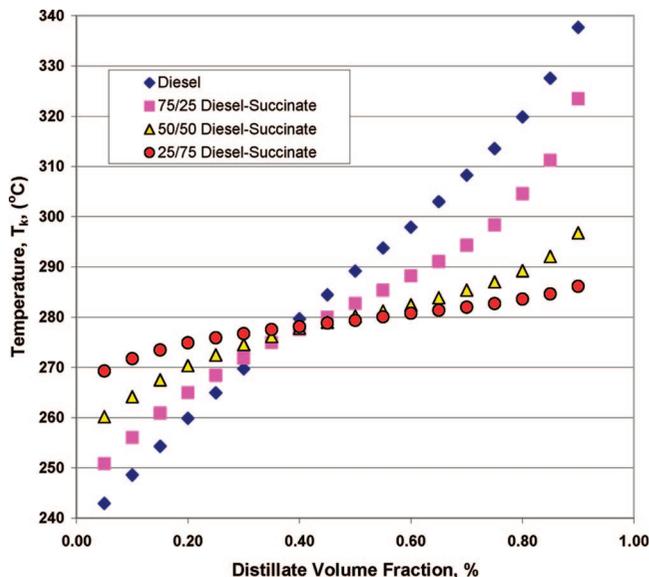


Figure 2. Distillation curves, presented in T_k , for diesel fuel and three mixtures of diesel fuel with dibutyl succinate (DBS). The uncertainties of the measurements are discussed in the text.

could represent the thermophysical properties (equilibrium and transport properties), then the properties can be calculated at any required temperature and pressure, and mixture behavior can be predicted. The soundness of this philosophy has been demonstrated, for example, with aviation fuels.³³ This will facilitate the design and optimization of process development for fuel production. Moreover, such data will facilitate the development of surrogate fuel testing for engine design and optimization, and the mitigation of pollutants such as particulates.

In earlier work, we described a method and apparatus for advanced distillation curve measurement that is especially applicable to the characterization of fuels. This method is a significant improvement over previous or classical approaches,³⁴ featuring (1) a composition explicit data channel for each distillate fraction (for both qualitative and quantitative analysis), (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state, (3) temperature, volume, and pressure measurements of low uncertainty suitable for equation of state development, (4) consistency with a century of historical data, (5) an assessment of the energy content of each distillate fraction, (6) trace chemical analysis of each distillate fraction, and (7) a corrosivity assessment of each distillate fraction.^{14,35–43} For diesel fuels, as with any fuel, the distillation curve is one of the main operational and design parameters used to ensure good engine performance

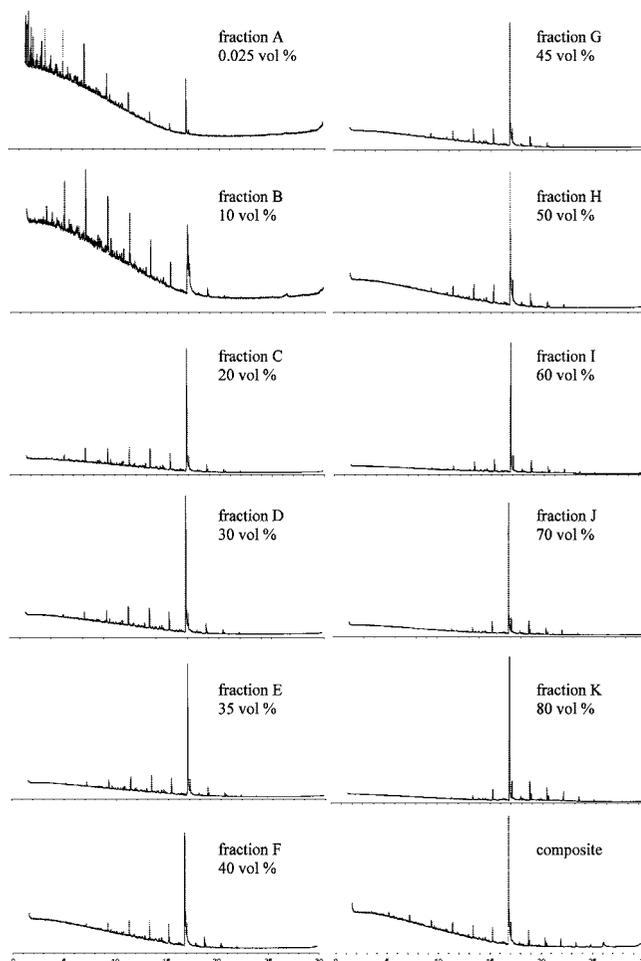


Figure 3. Typical chromatograms as a function of distillate volume fraction, measured with a flame ionization detector, for the 75/25 (vol/vol) mixture of diesel fuel with dibutyl fumarate.

and optimization. Moreover, it was recently cited as one of the properties most needed in the development of diesel fuel surrogates for advanced fuel research.⁴⁴

The advanced distillation curve approach provides important advantages over other methods such as the simulated distillation method embodied in procedures such as American Society for Testing and Materials (ASTM) D-2887. In that method, for example, one uses the gas chromatographic behavior of a suite of compounds as a frame of comparison with a fuel. The very significant advantage offered by the approach utilized in this paper is the ability to model the distillation curve resulting from our metrology with an equation of state. We have applied this

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Table 5. Summary of the Results of Hydrocarbon Family Calculations Based on the Modification of the ASTM D-2789 Method^a

volume fraction (%)	paraffins (vol %)	monocycloparaffins (vol %)	dicycloparaffins (vol %)	alkylbenzenes (vol %)
(a) 75/25 Diesel/Fumarate				
composite	46.2	33.4	10.4	10.0
0.025	36.7	29.0	7.4	27.0
10	40.3	29.3	9.8	20.7
20	43.6	30.1	10.6	15.7
30	44.2	30.9	10.8	14.1
35	45.3	31.2	10.9	12.7
40	46.3	31.9	10.4	11.4
45	46.5	32.0	10.9	10.6
50	47.8	32.6	10.5	9.1
60	46.0	31.5	11.8	10.6
70	47.1	32.1	11.8	8.9
80	45.8	31.5	12.3	10.3
residue	41.1	31.5	14.7	12.7
(b) 50/50 Diesel/Fumarate				
composite	48.0	33.4	11.0	7.6
0.025	39.7	35.2	6.4	18.7
10	42.6	30.0	10.8	16.7
20	45.7	31.5	10.3	12.5
30	48.3	32.2	10.1	9.3
35	48.2	32.5	10.3	9.0
40	47.1	32.0	11.2	9.6
45	48.6	32.6	11.0	7.8
50	49.5	33.1	10.8	6.6
60	49.7	33.5	11.5	5.3
70	51.2	34.0	10.4	4.3
80	50.3	33.8	11.0	4.9
residue	40.7	32.8	14.4	12.1
(c) 25/75 Diesel/Fumarate				
composite	48.9	32.8	11.6	6.7
0.025	43.0	34.8	7.2	15.0
10	48.1	33.2	9.6	9.1
20	51.4	34.0	9.3	5.3
30	51.2	34.1	9.8	4.9
35	50.8	34.2	10.6	4.5
40	50.8	34.1	10.7	4.4
45	48.2	38.7	10.4	2.6
50	54.7	30.7	11.7	2.9
60	51.6	34.5	10.7	3.2
70	51.9	34.5	10.9	2.7
80	52.4	35.5	10.1	2.0
residue	46.7	30.1	13.1	10.0
(d) 75/25 Diesel/Succinate				
composite	41.5	32.1	10.7	15.8
0.025	32.6	26.9	11.4	29.1
10	37.3	28.9	10.9	22.9
20	38.3	29.8	10.8	21.1
30	39.9	30.4	10.8	18.9
35	40.7	30.2	10.9	18.3
40	41.3	31.9	9.6	17.3
45	40.8	32.0	10.8	16.3
50	41.6	32.4	10.3	15.7
60	41.7	32.5	10.7	15.1
70	42.9	31.2	11.0	14.9
80	43.1	31.9	11.1	13.9
residue	39.3	30.4	15.4	14.9
(e) 50/50 Diesel/Succinate				
composite	41.0	32.8	10.3	15.9
0.025	33.5	31.4	8.8	26.3
10	39.3	30.5	10.0	20.3
20	39.8	31.8	9.9	18.5
30	40.8	32.6	9.2	17.4
35	41.2	33.4	9.0	16.5
40	41.5	33.5	8.8	16.2
45	42.0	34.6	8.5	15.0
50	43.0	33.5	8.4	15.1
60	42.9	34.0	8.7	14.4
70	43.0	34.0	8.5	14.5
80	42.9	34.7	8.6	13.9
residue	40.2	30.9	14.9	14.0
(f) 25/75 Diesel/Succinate				
composite	41.6	37.5	7.2	13.7
0.025	40.2	37.1	6.3	16.3
10	40.6	34.5	8.2	16.7
20	40.9	35.6	7.5	16.0
30	42.6	37.6	6.0	13.8
35	43.8	37.0	5.9	13.3
40	41.8	37.7	6.4	14.1
45	42.4	39.5	5.7	12.4
50	41.9	39.3	5.7	13.1
60	42.8	39.2	5.4	12.6
70	41.0	42.0	5.0	12.0
80	42.9	39.1	5.5	12.5
residue	39.8	30.6	14.8	14.7

^aIn this table, we have normalized over the paraffins, monocycloparaffins, dicycloparaffins, and aromatics only.

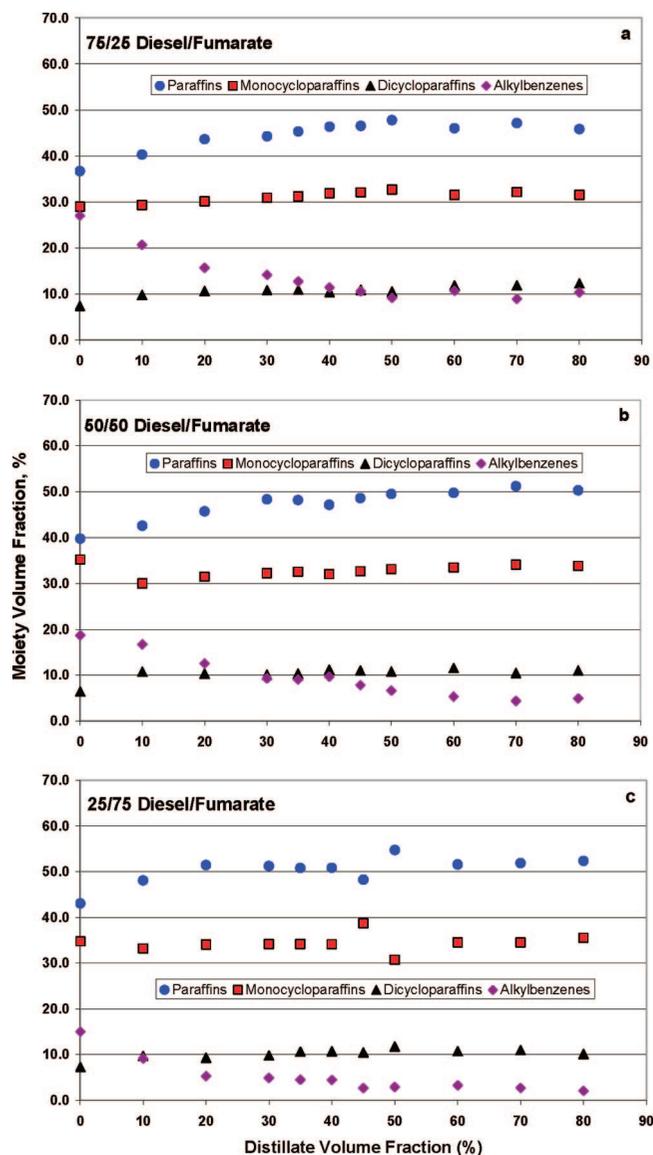


Figure 4. Results of the hydrocarbon type classification determination done with the modified D-2789 technique for mixtures of diesel fuel with dibutyl fumarate. The uncertainty is discussed in the text.

metrology to gasolines, diesel fuels, aviation fuels, rocket propellants, and crude oils. Clearly, it is not always needed or desirable to apply all aspects of the advanced distillation curve metrology in every application. For highly finished fuels such as the low sulfur diesel fuels that are used today (and measured in this work), for example, it is usually unnecessary to assess corrosivity as a function of distillate fraction.

Experimental Details

The petroleum derived diesel fuel used in this work was obtained from a commercial source and was stored at 7 °C to preserve any volatile components. No phase separation was observed as a result of this storage procedure. The fuel was a winter grade, low wax, ultralow sulfur diesel fuel that incorporated a red dye (specifying off-road use) and was refined locally from petroleum of the Denver–Julesburg field. This fluid was used without any purification or modification. The composition was studied with a gas chromatographic method (30 m capillary column of 5% phenyl–95% dimethyl polysiloxane having a thickness of 1 μm and a

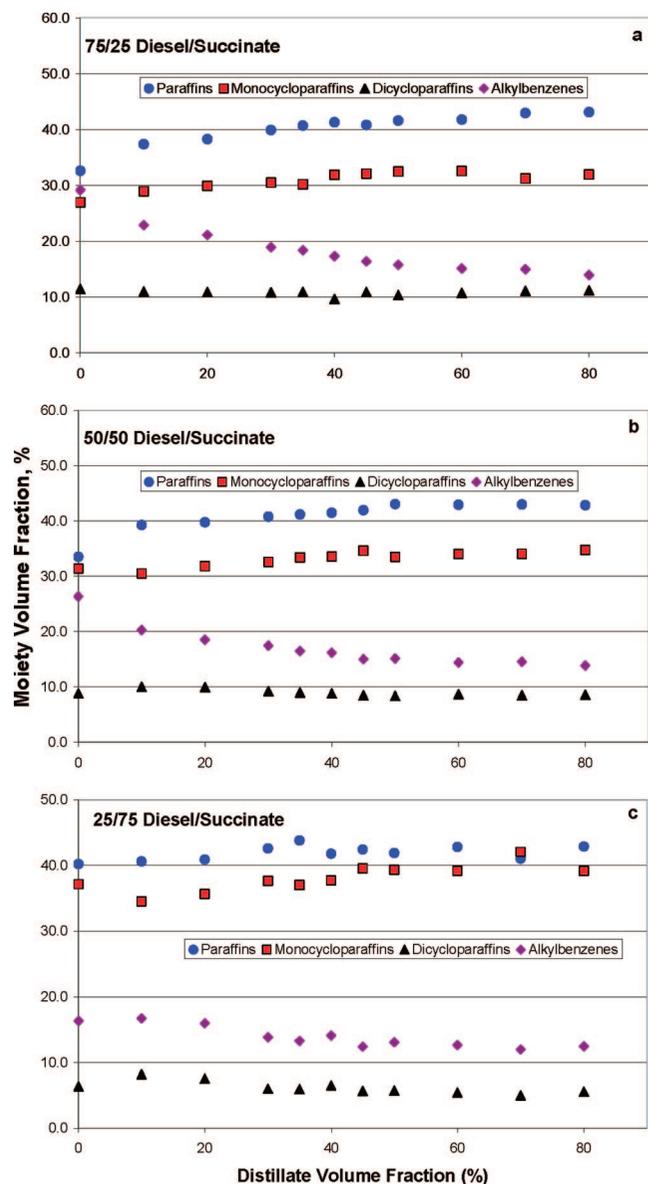


Figure 5. Results of the hydrocarbon type classification determination done with the modified D-2789 technique for mixtures of diesel fuel with dibutyl succinate. The uncertainty is discussed in the text.

temperature program from 90 to 275 °C, 9 °C/min) using flame ionization detection and mass spectrometric detection.^{45,46}

The dibutyl succinate (DBS) and dibutyl fumarate (DBF) were obtained from commercial sources and were used without additional purification. Representative properties of these fluids are provided in Table 1. The purity of these fluids was verified with a chromatographic method similar to that specified above for the diesel fuel. The purity of the DBS was found to be approximately 98% (mass/mass), with 11 impurity peaks being detected by GC-MS. Not all of the 11 impurity peaks that were present could be identified. Small quantities of dibutyl peroxide (CAS No. 3849-34-1), the trans isomer of DBF (CAS No. 105-76-0), (Z)-9-octadecanoic acid methyl ester (methyl oleate, CAS No. 112-62-9), and 9,12-octadecadienoic acid methyl ester (methyl linoleate, CAS No. 2566-97-4) were identified. The DBF was found to contain approximately 0.2% (mass/mass) of dibutyl maleate (that is, the cis isomer having the same molecular formula) and 0.5% of

2-hydroxy-butanedioic acid dibutyl ester (CAS No. 6280-99-5). These fluids are closely related to DBF and will not affect the mixture properties to a significant extent. As with DBS, the purity of the fluid is certainly adequate for the measurements presented here. A moisture analysis was done with Karl Fisher Coulombic titrimetry. No more than 10 ppm (mass/mass) water was found. Care was taken in the handling of these fluids to minimize the uptake of moisture during the mixture preparation and measurement of the distillation curves.

The *n*-hexane used as a solvent in this work was obtained from a commercial supplier and was analyzed by gas chromatography (30 m capillary column of 5% phenyl–95% dimethyl polysiloxane having a thickness of 1 μm and a temperature program from 50 to 170 °C, 5 °C/min) using flame ionization detection and mass spectrometric detection. These analyses revealed the purity to be approximately 99.9%, and the fluid was used without further purification.

The distillation curve apparatus has been described in detail earlier. The distillation flask is a 500 mL round-bottom flask that is placed in a two-part aluminum heating jacket, the lower part of which is contoured to fit the flask. Above the distillation flask, a centering adapter provides access for two thermally tempered J-type thermocouples that enter the distillation head. One thermocouple enters the distillation flask and is submerged in the fluid, to monitor the temperature of the bulk fluid. This temperature is referred to as T_k (signifying its measurement in the kettle). The other thermocouple is centered at the low point of distillate takeoff (the typical distillation head placement, as recommended graphically in ASTM D-86). This temperature is referred to as T_h (signifying its measurement in the distillation head). Both of the thermocouples were calibrated in an indium triple point cell traceable to a National Institute of Standards and Technology (NIST) standard. The other major features of the apparatus, including the level-stabilized receiver, the sampling adapter, the model predictive temperature controller, and the vortex tube chilling of the condenser, are unchanged from previous reports.

The mixtures of the diesel fuel with the oxygenating fluids were prepared volumetrically in graduated mixing cylinders that had an uncertainty of 0.1 mL. For each oxygenate blend, mixtures with 75, 50, and 25% diesel fuel (vol/vol) were prepared. The differing physical properties of the hydrocarbon species in diesel fuel and the various oxygenates were apparent during the preparation of the mixtures. The hydrocarbon mixture in diesel fuel typically has a density of 0.75–0.85 g/mL, while the density of the oxygenate compounds is much higher, approximately 0.96 g/mL. The oxygenate was observed to immediately sink to the bottom of the mixing cylinder. Once mixed, there was no tendency for the two species (diesel fuel or oxygenate) to demix or separate. As with the synthetic oxygenate mixtures presented previously, we realize that not all of these mixtures may be practical choices for fuel blends. Our mixtures were chosen to cover as large a range of composition as practical for the purpose of modeling the results with equations of state in the future.

Since the measurements of the distillation curves were performed at ambient atmospheric pressure (measured with an electronic barometer), temperature readings were corrected for what should be obtained at standard atmospheric pressure. This was done with

(47) Standard test method for hydrocarbon types in low olefinic gasoline by mass spectrometry, ASTM Standard D 2789-04b. *Book of Standards*; American Society for Testing and Materials: West Conshohocken, PA, 2005; Vol. 05.01.

(48) Frenkel, M.; Chirico, R. D.; Diky, V.; Muzny, C.; Lemmon, E. W.; Yan, X.; Dong, Q. *NIST Standard Reference Database 103, NIST ThermoData Engine (TDE)*; version 2.0, National Institute of Standards and Technology: Gaithersburg, MD, 2006.

(49) Lemmon, E. W.; Huber, M. L.; McLinden, M. O. *REFPROP, Reference Fluid Thermodynamic and Transport Properties (NIST Standard Reference Database 23)*; version 8, National Institute of Standards and Technology: Gaithersburg, MD, 2007.

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(45) Bruno, T. J.; Svoronos, P. D. N. *CRC Handbook of Basic Tables for Chemical Analysis*, 2nd ed.; Taylor and Francis CRC Press: Boca Raton, 2004.

(46) Bruno, T. J.; Svoronos, P. D. N. *CRC Handbook of Fundamental Spectroscopic Correlation Charts*; Taylor and Francis CRC Press: Boca Raton, 2005.

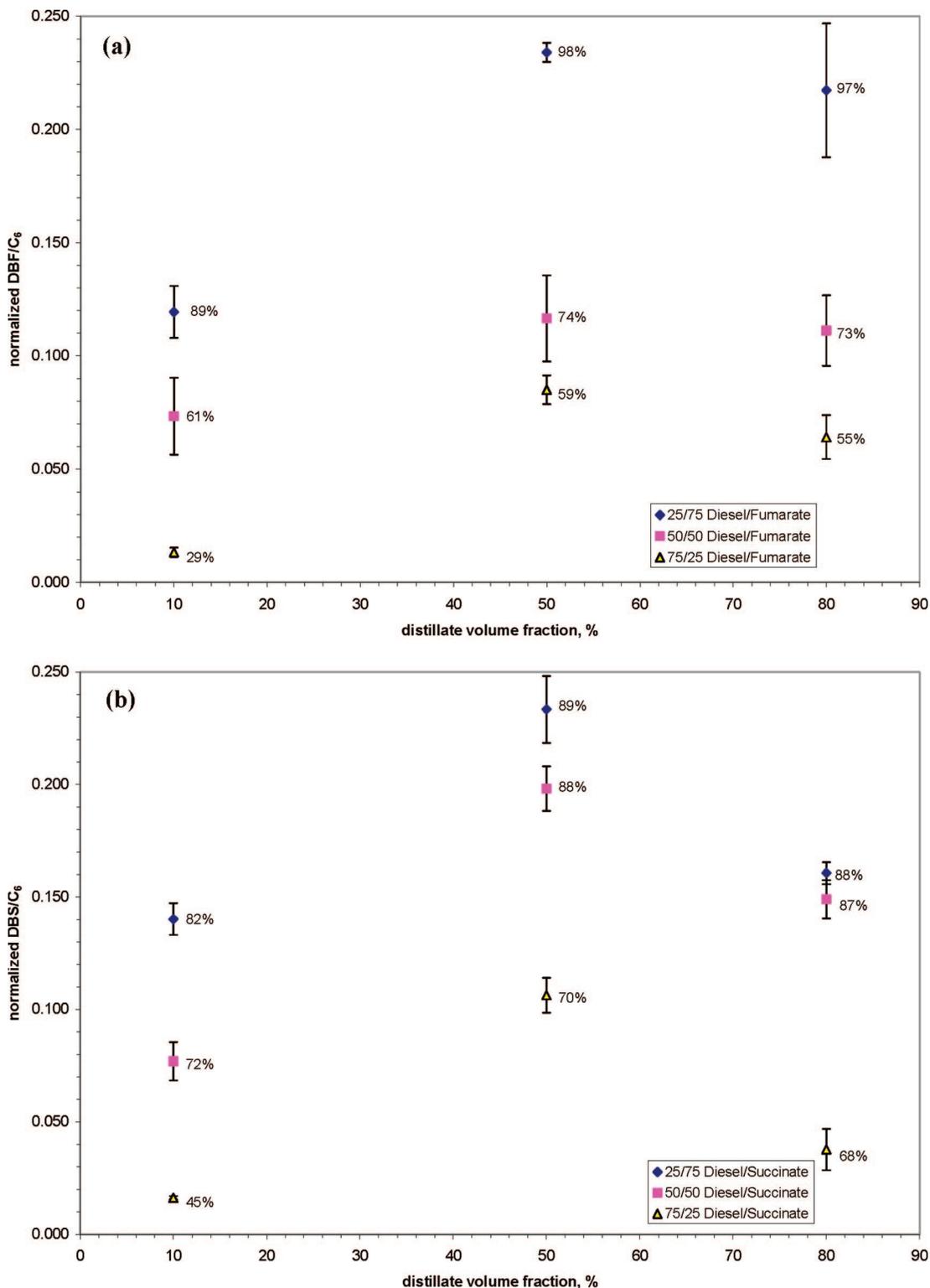


Figure 6. (a) Ratio of the area count intensity of the peak for dibutyl fumarate relative to that of the solvent *n*-hexane. (b) Ratio of the area count intensity of the peak for dibutyl succinate relative to that of the solvent *n*-hexane.

the modified Sydney Young equation, in which the constant term was assigned a value of 0.000 109.³⁵ This value corresponds to a carbon chain of 12. In the chemical analysis of the diesel fuel sample (see above), as well as in previous work on diesel fuel, it was found that *n*-dodecane can indeed represent the fluid as a very rough surrogate. The magnitude of the correction is of course dependent upon the extent of departure from standard atmospheric pressure. The location of the laboratory in which the measurements reported herein were performed is approximately 1650 m above sea level, resulting in a typical temperature correction of 7 °C. The actual

measured temperatures are easily recovered from the Sydney Young equation at each measured atmospheric pressure.

Results and Discussion

Initial Boiling Temperatures. During the initial heating of each sample in the distillation flask, the behavior of the fluid was observed. Direct observation through the flask window or through an illuminated bore scope typically allows measurement of the onset of boiling for each of the mixtures. During the

early stages of a measurement the first bubbles will appear intermittently, and this action will quell if the stirrer is stopped momentarily. Sustained vapor bubbling is then observed. In the context of the advanced distillation curve measurement, sustained bubbling is also somewhat intermittent, but it is observable even when the stirrer is momentarily stopped. Finally, the temperature at which vapor is first observed to rise into the distillation head is observed. This is termed the vapor rise temperature. The measurements of the vapor rise temperatures are important because they are the initial boiling temperatures (IBT) of each fluid. Moreover, these temperatures can be modeled theoretically, for example, with an equation of state.

The dark red dye present in the diesel fuel sample that we used prevented a measurement of the onset of bubbling and the sustained bubbling temperatures in the mixtures studied in this work. Fortunately, the vapor rising temperature could still be determined. These measurements, presented as averages of three separate determinations, are provided in Table 2. The uncertainty in the vapor rise temperature is approximately 0.2 °C. As we have noted for all other fluids measured with the advanced approach, the IBT values we have presented are very different from those that would be obtained with the classical method which are systematically in error.

While the vapor rising temperatures of the analogous mixtures of diesel fuel with either DBF or DBS are very close to one another, the mixtures with DBF show initial boiling temperatures slightly higher than those of the mixtures with DBS. This is consistent with the boiling temperatures of the pure oxygenating fluids provided in Table 1. As we will discuss below, this is also consistent with the temperature behavior of the distillation curves that were measured.

Distillation Curves. Representative distillation curve data for the samples of mixtures of diesel fuel and the biomass-derived oxygenating fluids, presented in both T_k (measured directly in the fluid) and T_h (measured in the distillation head), are provided in Table 3 and 4. The T_k data are true thermodynamic state points while the T_h data allows comparison with earlier measurements. In this table, the estimated uncertainty (with a coverage factor $k = 2$) in the temperatures is 0.1 °C. We note that the experimental uncertainty of T_k is always somewhat lower than that of T_h , but as a conservative position, we use the higher value of uncertainty for both temperatures. The uncertainty in the volume measurement that is used to obtain the distillate volume fraction is 0.05 mL in each case. The uncertainty in the pressure measurement (assessed by logging a pressure measurement every 15 s for the duration of a typical distillation) is 0.001 kPa. The relatively low uncertainties in the measured quantities facilitate modeling the results, for example, with an equation of state. The same distillation curve data are provided graphically in Figures 1 and 2. The shapes of all of the curves are of the subtle sigmoid type that one would expect for a highly complex fluid with many components, distributed over a large range of relative molecular mass.

The distillation curves of the diesel fuel mixtures with DBS and DBF are strikingly similar to those presented earlier for DBM. The mixtures (with increasing volume fractions of oxygenate) are progressively less volatile than diesel fuel (at the start of the distillation curves), and the distillation curves begin at higher temperatures than those for diesel fuel alone. Moreover, as with the mixtures with DBM, the slope becomes less pronounced (approaching a straight line in temperature) as the quantity of either DBS or DBF increases. For the 25/75 mixture of either fluid, we see the mixture with diesel fuel tending toward pure fluid behavior.

We can examine the average difference of T_k and T_h as a measure of this trend; the convergence of these two temperatures for pure fluids has been demonstrated previously.⁴¹ Indeed, for azeotropic mixtures, we have noted that the difference can vanish, within experimental uncertainty. For DBS, we obtain the following: diesel fuel 26.4 °C; diesel fuel mixed with DBS 75/25 11.4 °C; 50/50 7.1 °C; 25/75 3.5 °C. For DBF, we obtain the following: diesel fuel 26.4 °C; diesel fuel mixed with DBF 75/25 19.1 °C; 50/50 9.4 °C; 25/75 6.1 °C. These temperature trends are consistent with a mixture that is becoming less complex and is approaching a pure fluid.

We observe a crossover point in the distillation curves (at distillate volume fraction of approximately 40%) at which the volatility trends of the curves reverse. Thus, in the latter stages of the distillation, the heavier components in diesel fuel predominate in the resulting mixtures and the curves display a lower volatility as the diesel fuel concentration increases. This is the same behavior that was noted with DBM.

The difference in the distillation curve behaviors of the mixtures of diesel fuel with the succinate and fumarate is very subtle but still observable. We note that for each fraction of the three mixtures of DBS and DBF, the distillation temperatures for DBF are somewhat higher, and this observed difference increases with increasing concentration of the oxygenate fluid. Thus, for the 75/25 mixture rich in diesel fuel, the difference is, on average, 2.9 °C, increasing to 5.9 °C for the 50/50 mixture, and to 7.4 °C for the 25/75 mixture. When compared to the synthetic fluid DBM (presented previously), mixtures with DBS are only slightly higher in average distillation temperatures. For most of the fractions, the differences are within the experimental uncertainty.

Composition Channel Information. *Analysis of Distillate Fractions.* While the gross examination of the distillation curves is instructive and valuable for many design purposes, the composition channel of the advanced approach can provide even greater understanding and information content. One can sample and examine the individual fractions as they emerge from the condenser, as discussed in the introduction. Following the analytical procedure described in the experimental section, samples were collected and prepared for analysis. Chemical analyses of each fraction were done by gas chromatography with flame ionization detection and mass spectrometric detection. Representative chromatograms (measured by flame ionization detection) for each fraction (A–K) of the 75/25 (vol/vol) mixture of diesel fuel with the DBF are shown in Figure 3. Also provided is the starting fluid, which is labeled as the composite. The solvent front (for *n*-hexane), which elutes at the start of the chromatographic analysis, has been deleted from these chromatograms for clarity of presentation. This is a typical set of chromatograms obtained from the composition channel. The scales of the individual chromatograms are normalized to the largest peak. The time axes are from 0 to 30 min for each chromatogram, and the abundance axis is presented in arbitrary units of area counts (voltage slices) for each chromatogram. It is clear that, although there are many peaks on each chromatogram (30–40 major peaks and 60–80 minor and trace peaks), these chromatograms are much simpler than that of the starting or composite fluids, which can contain 300–400 peaks.

Fraction A on the chromatogram represents a distillate volume fraction of 0.025%; this fraction is clearly mostly diesel fuel, with a small quantity of DBF present at a retention time of approximately 16.5 min. As the distillation proceeds, the DBF peak grows in each chromatogram to become the dominant constituent. In each of the subsequent chromatograms, one can

see the diesel fuel constituents progress to longer retention times, indicative of progressively heavier constituents being distilled. This figure illustrates just one chemical analysis strategy that can be applied to the distillate fractions. It is possible to use any analytical technique that is applicable to solvent-borne liquid samples that might be desirable for a given application.

Hydrocarbon Type Classification. The distillate fractions of the diesel fuel and the mixtures of diesel fuel with DBF and DBS oxygenates were examined for hydrocarbon types by use of a mass spectrometric classification method summarized in ASTM Method D-2789.⁴⁷ In this method, one uses mass spectrometry (or gas chromatography–mass spectrometry) to characterize hydrocarbon samples into six types. The six types or families are paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes (arenes or aromatics), indanes and tetralins (grouped as one classification), and naphthalenes. Although the method is specified only for application to low olefinic gasolines and it has significant limitations, it is of practical relevance to many complex fluid analyses and is often applied to gas turbine fuels, diesel fuels, rocket propellants, and missile fuels. The uncertainty of this method and the potential pitfalls were treated earlier.³⁶ As discussed above, the solutions were prepared from withdrawn 7 μL samples of distillate fraction that were dissolved in a known mass of solvent (*n*-hexane). This solvent was chosen because it causes no interference with the sample constituents. For the hydrocarbon type analysis of the distillate fraction samples, 1 μL injections of these solutions were made into the GC-MS. Because of this consistent injection volume, no corrections were needed for sample volume.

For the work on mixtures with DBF and DBS presented in this paper, we had to modify the usual calculation to exclude two of the families listed above: the indanes/tetralins and the naphthalenes. The mass spectra of DBF and DBS have appreciable fragmentation peaks at $m/z = 103, 104, 117, 118, 145, 155, 156, \text{ and } 159$. Since these mass spectral peaks are important in the indane/tetralin and naphthalene families and their analysis and determination by method D-2789 is compromised, the interference prevents a reliable calculation. For this work, these peaks were excluded and the mass spectral peaks simply normalized without them. This change in the usual procedure, as well as the presence of ether and ester groups on the DBF and DBS, renders the results from D-2789 approximate only.

The results of the modified D-2789 analysis discussed above type analyses for mixtures with DBS and DBF are presented in Table 5a–f and Figures 4 and 5. All of the distillate fractions presented in the table were measured in the same way (m/z range from 15 to 550 relative molecular mass units gathered in scanning mode, each spectrum corrected by subtracting trace air and water peaks).

The behavior exhibited in these analyses can be examined in two ways, both of which are instructive. One can examine the compositional trends as a function of increasing oxygenate concentration (across the same fraction) or as a function of distillate fraction. In general, as the concentration of the oxygenate increases, the paraffinic content increases as the distillation proceeds. For mixtures that contain 75% (vol/vol) of oxygenate, the paraffinic content is nearly constant through the distillation. The paraffinic moieties present on the oxygenate molecules ensure this constancy, despite the fact that glycol esters are not paraffins. The same behavior is observed for the monocyclics and dicyclics, but at a lower total level.

The variation of the aromatics is particularly interesting, however. The mutagenicity of a diesel fuel is negatively correlated with the later parts of the distillation curve and

positively correlated with the aromatic content of the fuel. To a lesser extent, the mutagenicity is also negatively correlated with the naphthalenics in the fuel. Moreover, carbon particulate emission indices correlate with the aromatic content of the later fractions of the distillation curve. For diesel fuel, the concentration of aromatic species is seen to decrease as the distillation proceeds. This is the same behavior found with aviation fuels, but with gasolines, the opposite was observed. Here, with oxygenated mixtures of diesel fuel, the aromatic concentration is always diluted in the presence of the glycol ethers. The combination of the distillation curves with this composition information is useful for fuel design since one can simultaneously track the volatility and aromatic content.

Oxygenate Concentration As a Function of Distillate Cut. Another application of the composition channel of data is in tracking the oxygenate content through the course of the distillation. We can demonstrate this by an analysis of the sampled distillate fractions, corrected for sample size. We must correct for sample size because it is not possible to withdraw exact 7 μL aliquots of distillate during the measurement of the distillation curve. The presence of the hexane solvent provides a convenient way to standardize for sample size, however, since this varies very little from sample to sample. As we see in Figure 3, the concentration of the oxygenate increases after the commencement of the distillation and becomes the dominant constituent. In the later stages of the distillation, however, the heavier constituents of diesel fuel are seen at higher retention times, and the oxygenate fluid shows a trend toward lower concentrations. We can show this quantitatively in Figure 6a and b. In Figure 6a, we present the ratio of the area counts of dibutyl fumarate relative to the solvent *n*-hexane for the 10, 50, and 80% distillate fraction. We note that the ratio increases as expected as the oxygenate concentration increases from 25 to 50 and finally to 75% (vol/vol). The relatively high uncertainty in some of the ratios is the result of uncertainty in sample size. The sample size uncertainty is the unavoidable result of taking samples of flowing distillate manually with a syringe that is not temperature controlled. We note that the ratio appears to reach a maximum in the central part of the distillation curve. This is the point at which the oxygenate concentration is highest. After this point, the trend is downward, as the oxygenate is depleted, and the heavier components of diesel fuel begin to predominate. The same observations apply to the mixtures of diesel fuel with dibutyl succinate, presented in Figure 6b.

Conclusions

In this paper, we have presented the results of our composition explicit distillation curve measurements performed on diesel fuel and a series of diesel fuel oxygenates prepared with glycol esters that can be bioderived: dibutyl fumarate and dibutyl succinate. The measurements are significant since the thermodynamic consistency of the new distillation curve measurement allow the temperature data to be modeled with an equation of state and used for fuel design and optimization, as well as for the development of surrogates. We note the same kind of crossover behavior with DBF and DBS that we previously observed with mixtures of diesel fuel with dibutyl maleate. Finally, we demonstrated how the composition explicit data channel was used to track the changes in fuel components across the distillation range.